Chapter (2)

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SI Units

SI Units

Constant	Symbol	Value in SI Units	Value in c.g.s units
Avogadro's constant	N_A	6.022×10^{23} mol^{-1}	6.022×10^{23} mol^{-1}
Planck's constant	h	6.026×10^{-34} J s	6.026×10^{-27} erg s
Boltzmann constant	K	1.3806×10^{-23} J K^{-1}	1.3806×10^{-16} erg K^{-1}
Gas constant	R	8.3144 J K^{-1} mol^{-1} 0.082 L atm mol^{-1} K^{-1}	1.987 cal K^{-1} mol^{-1}
Atmospheric pressure	P	1.01325×10^5 N m^{-2}	1 atm
Acceleration	g	9.80665 m s^{-2}	--
Gravitational constant	G	6.672×10^{-11} N m^2 Kg^{-2}	--
Speed of light	c	2.9979×10^8 m s^{-1}	2.9979×10^{10} cm s^{-1}

1cal = 4.184 J =4.184 x 10^{-7} erg = 41.293 atm cm^3

1 N = 10^5 dynes

1 J = 10^7 ergs = 0.239 cal

1 eV = 1.602 x 10^{-19} J = 1.6021 x 10^{-12} erg molecule^{-1}

= 96.48 kJ mol^{-1} = 23.06 kcal mol^{-1}= 8065.5 cm^{-1}

1 atm = 760 mm Hg = 760 Torr = 101325 N m^{-2} = 101.325 kPa

1 bar = 10^5 Pa = 0.987 atm

1 L = 10^3 cm^3 = 1 dm^3

1A°= 10^{-8} cm = 10^{-10} m

Kelvin = Tc° + 273

Thermodynamics

Introduction

The word "thermodynamics" implies flow of heat, it deals with energy changes accompanying all types of physical and chemical process. Thermodynamics based on two laws are first and second laws of thermodynamics.

The laws of thermodynamics apply only to matter in bulk and not to individual atoms or molecules. Thermodynamics can only predict weather a given process which include a chemical reaction and it does not tell anything about the rate at which a given process may proceed.

For example:

Thermodynamics predict that hydrogen and oxygen gases would react at ordinary temperature to yield liquid water. But it does not tell weather the reaction would be fast or slow.

Types of thermodynamics

1) Classical thermodynamics

Deals with the microscopic properties of the matter, It deals with the properties of aggregates of vast numbers of microscopic particles (molecules, atoms, and ions). classical thermodynamics treats matter as a continuous material medium rather than as the collection of discrete microscopic particles we know are actually present.

2) Statistical thermodynamics

Is a branch of science which is based on statistical mechanics (it acts as bridge between thermodynamics and quantum mechanical) and deals with the calculation of thermodynamic properties of matter from the classical or quantum mechanical (provide information about the energy of molecular system) behavior of a large congregation of atom or molecules.

Terminology of Thermodynamics

1) **System**

   Defined as any specified portion of matter under study which is separated from the rest of universe with a bounding surface. A system may consist of one or more substances

2) **Surroundings**

   The rest of the universe which might be in a position to exchange energy and the matter with the system.
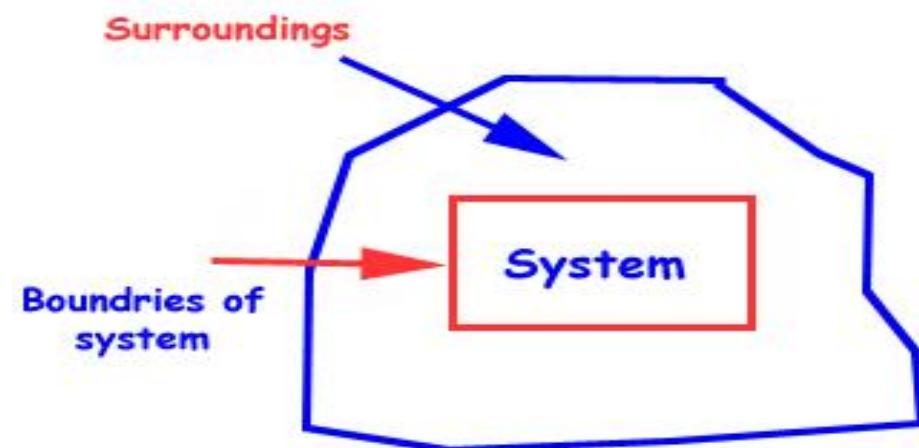
Fig.(a)

Types of Systems

1) Isolated system:

A system can exchange neither energy nor matter with its surroundings .

2) Closed System: A system which can exchange energy but not matter.
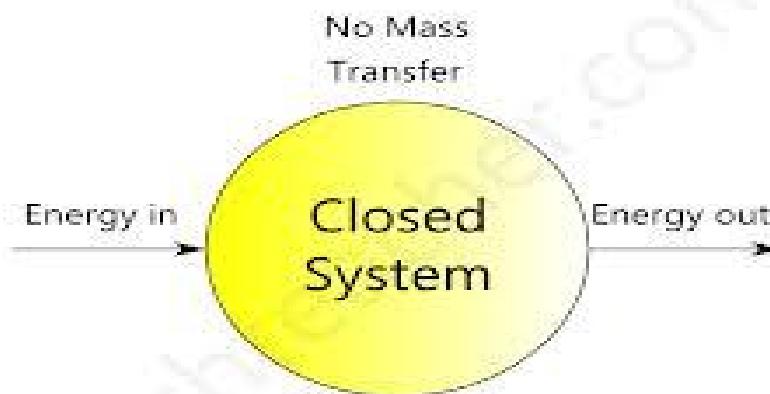
Fig.(b)

3) Open System:

A system which can exchange matter as well as energy with its surroundings.
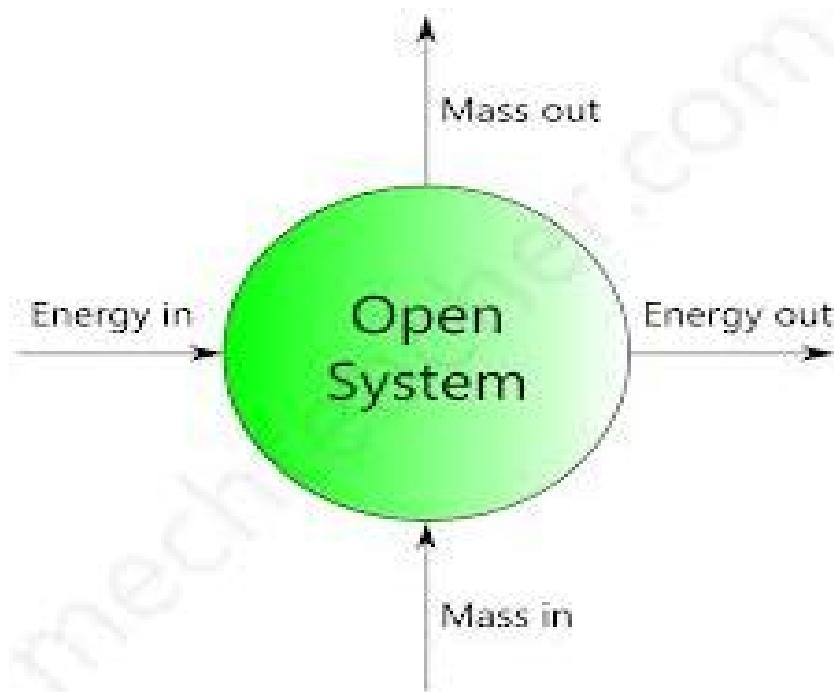
Fig.(c)

Terminology of Thermodynamics

4) Homogeneous System: It involves only one phase, for example, pure solid.

5) Heterogeneous System: It involves two or more phases separated from each other by interfacial boundaries, for example, two or more immiscible liquids.

Terminology of Thermodynamics

Properties of a System

Extensive properties:

An extensive property of system is that which depends upon the number of moles, volume, mass, energy, internal energy, ΔG, ΔH, ΔS…etc

Intensive properties:

An intensive property of system is that which independent of the of the substance present in the system, the examples are temperature, pressure, refractive index, density, viscosity , surface tension..etc.

Terminology of Thermodynamics

Thermodynamical Equilibrium

A system in which the microscopic properties do not under go any change with time.

Thermodynamic equilibrium implies the existence three kinds of equilibria in the system which are:

1) Thermal equilibrium:

It is system there is no flow of heat from one portion of system to another. This is possible if the temperature remains same throughout in all parts of the system.

2) Mechanical equilibrium:

It involves no flow of current of matter within the system or no mechanical work is done by one part of the system on another part of system. This is possible if the pressure remains same throughout in all parts of the system.

Terminology of Thermodynamics

3) Chemical equilibrium:

If the chemical composition of a system is not spontaneously changing with time, it is in a state of chemical equilibrium.

Terminology of Thermodynamics

Thermodynamic process:

The operation by which a system changes from one state to another state is called process.

The following types of processes are known:

1) Isothermal process ($\Delta T = 0$):

The process which occurs at constant temperature is called Isothermal process. And system exchanges heat with surrounding.

2) Adiabatic process (q=0):

When a process is carried out under such conditions that no exchange of heat takes place between the system and its surrounding (i.e. thermally insulated from the surrounding) is called Adiabatic process.

3) Isobaric process ($\Delta P = 0$):

If the pressure of the system remains constant during each step of the change in the state of the system is called Isobaric process.

4) Isochoric process ($\Delta V = 0$):

If the volume of the system remains constant during each step of the change in the state of the system is called Isochoric process.

PV diagrams
The different types of change can be illustrated on a PV diagram.
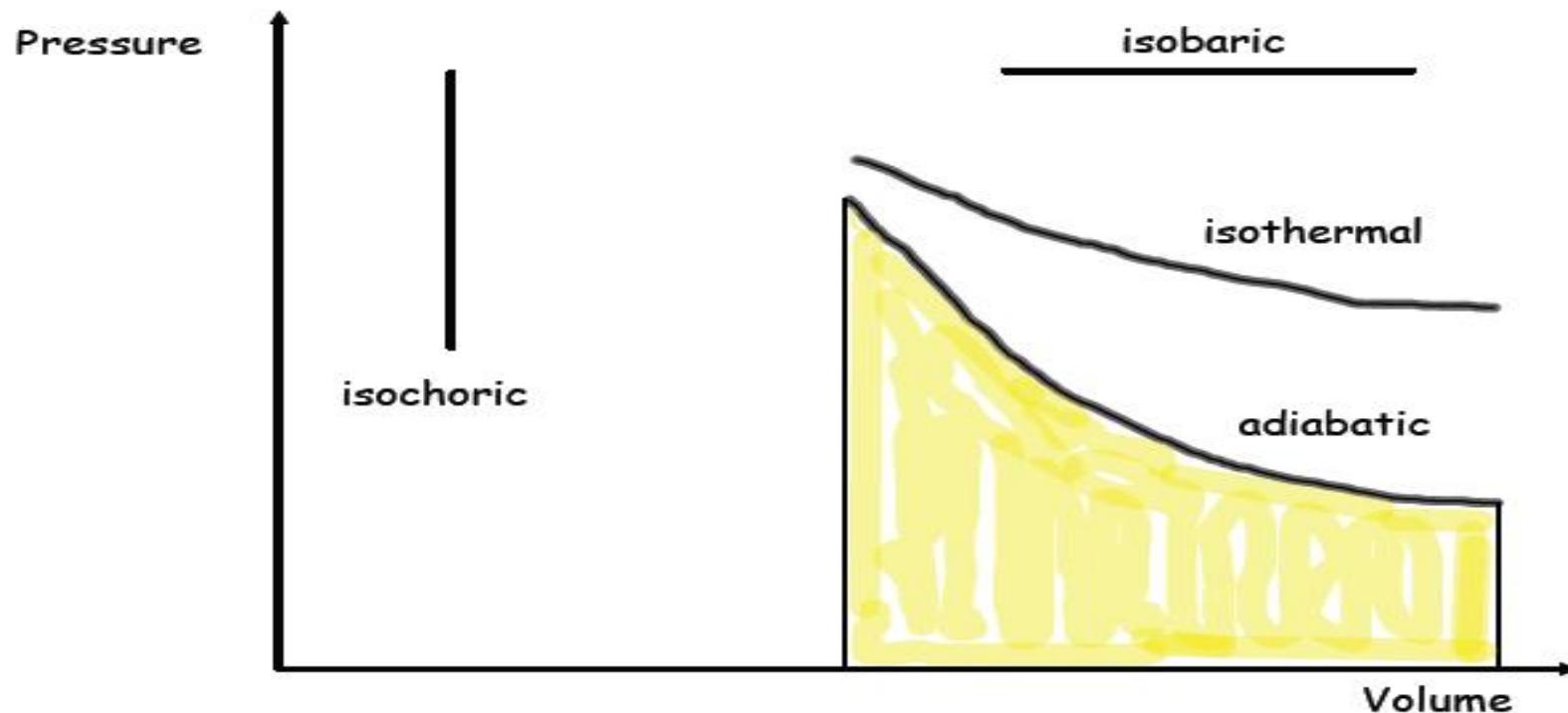
The work done is equal to the area under the line (W = P V)

$$W = P\Delta V = P(V_f - V_i)$$

In *Isochoric process* Work Done = 0.

Reversible and Irreversible Processes

Reversible Process

It is a process carried out infinitesimally slowly so that the driving force only infinitesimally greater than the opposing force. Reversible process cannot be realized in practice because it would require infinity time for it completion.

Irreversible Processes

It is a process which does not take place infinitesimally slowly.

The following example may be given to illustrate the difference between reversible and irreversible processes.

Consider a cylinder provided with an air-tight, weightless, frictionless piston, containing in it a certain quantity of a gas, as shown in a (Fig.1).
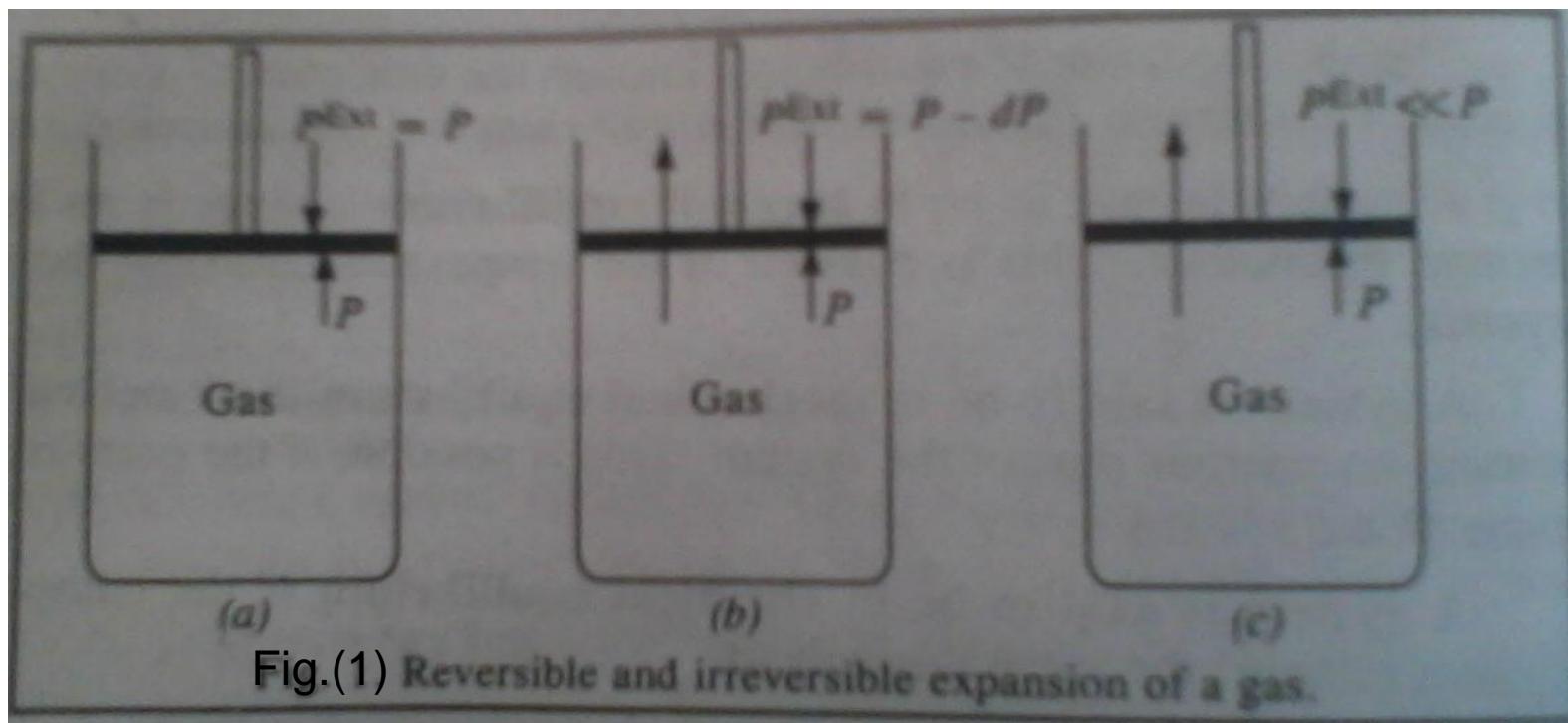
Fig.(1) Reversible and irreversible expansion of a gas.

Let the pressure P (external pressure) on the piston be exactly equal to the pressure of the gas within. The piston will neither move downward nor upward and consequently, there will be no change in the volume of the gas as shown in a (Fig.1a).


Fig.(1a)
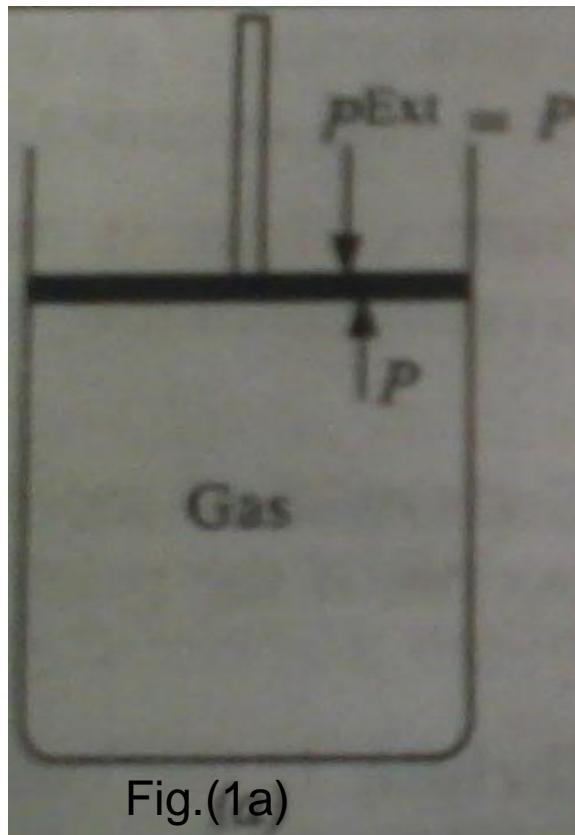
Now, suppose the pressure on the piston is decreased by an infinitesimally small amount dP. The pressure on the piston being P-dP, is now infinitesimally smaller than the pressure of the gas P within the cylinder as shown in a (Fig.1b). Hence, the piston will move up and the gas will expand by an infinitesimally small amount. If the pressure on the piston is kept infinitesimally smaller than the pressure of the gas itself, the expansion of the gas will continue infinitesimally slowly, (i.e. in a thermodynamically reversible manner).

Fig.(1b)
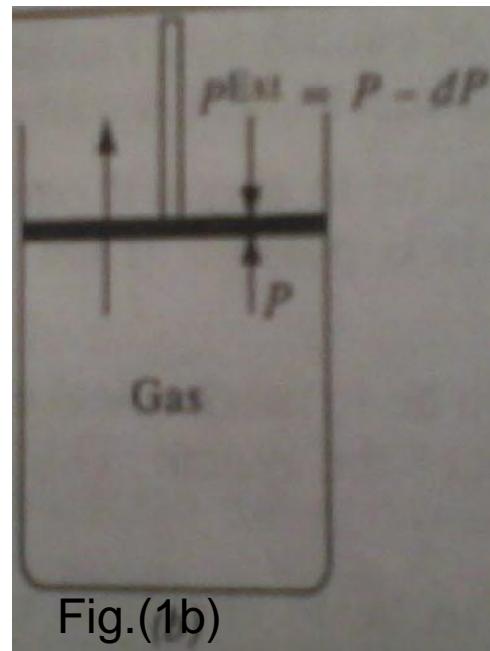
Reversible and Irreversible Processes

If the pressure on the piston (external pressure) is made much smaller than the pressure of the gas within the cylinder, the gas will expand rapidly, pushing the piston upward suddenly as shown in a (Fig.1c). The expansion of the gas in this case said to take place irreversibly.

Fig.(1c)
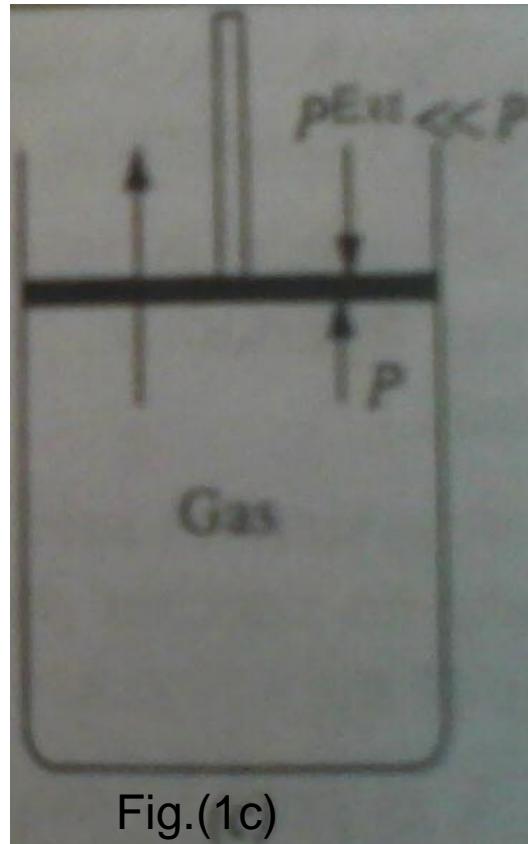
Spontaneous process

A process in which all steps cannot be retraced by themselves and take place without external interference of any kind. For example, when a bar of metal, hot at one end and cold at the other end is taken, the heat will be conducted by itself along the bar from hot to cold end until the temperature becomes uniform.

Energy (E)

Defined as the capacity for doing work.

Kinds of energy

1) kinetic energy: kinetic energy of a body due to motion.

2) Potential energy: potential energy of a body due to its position in space (structure of the molecules or its configuration with respect each other).

Total Energy = Kinetic Energy + Potential Energy

$$E = E_K + E_P$$

In SI system the unite for energy expressed in J or kJ.

Work (W)

Defined as

any quantity of energy that flows across the boundary between the system and surroundings which can be used to change in height of a mass in the surroundings.

Or

Defined as force multiplied by distance

$$dW = Fds$$

In SI system the unite for work expressed in J or kJ

Work (W)

Some types of work

1) Gravitational work:

This work is said to be done when a body is raised through a certain height against the gravitational field.

2) Electrical work:

It is done when a charged body moves from one potential region into another

3) Mechanical work:

It is associated with change in volume of a system against an external pressure.

Heat (Q)

Defined as

the quantity of energy that flows across the boundary between the system and surroundings because of a temperature difference between the system and surroundings.

$$Q = IVt$$

I = current (Ampere) , V = volt and t = time

In SI system the unite for work expressed in J or kJ.

Positive and Negative Heat and Work

Heat

Heat transferred _in to the system_ is positive •

Qin is +ve •

Heat transferred _out of the system_ is negative •

Qout is -ve •
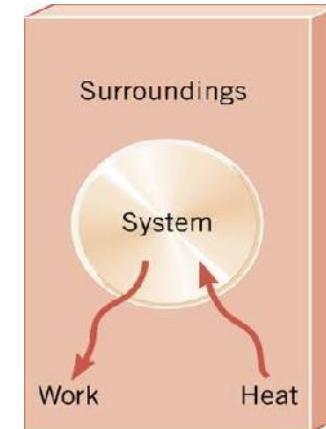
Fig.(a)

Work

- **Work done _on_ the system increases energy of the system.**

  - W_{in} **is +ve**

- **Work done _by_ the system decreases energy of the system.**

  - W_{out} **is -ve**
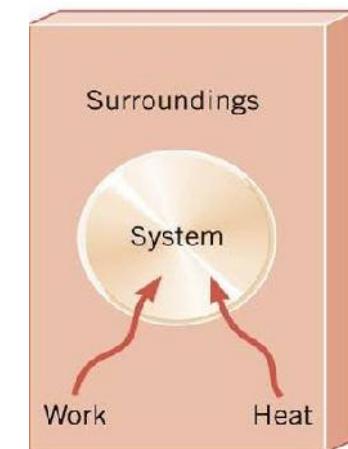
Fig.(b)

Internal energy (also called thermal energy) (U)

Defined as

the amount of energy which depends upon its chemical nature as well as upon

its temperature, pressure and volume.

Internal energy can take on a number of forms such as:

1) The kinetic energy of molecules.

2) The potential energy of the constituents of the system.

3) The internal energy stored in form of molecular vibrations and rotations.

4) The internal energy stored in form of chemical bonds can be released through

a chemical reactions

$$\Delta U = U_{final} - U_{initial}$$

ΔU change in the internal energy

Internal energy (also called thermal energy) (U)

i) If work is done by the surroundings on system (as during the compression of a gas)

Change in internal energy	=	Energy supplied to system as heat	+	Energy supplied to system as work

$$\Delta U = q \text{ (heat)} + w \text{ (work)}$$

ii) If work is done by the system on the surrounding (as during the expansion of a gas)

Change in internal energy	=	Energy supplied to system as heat	-	Energy supplied to system as work

$$\Delta U = q \text{ (heat)} - w \text{ (work)}$$

We have found for a monoatomic gas
$$U = 3/2 \, n \, R \, T$$

From a PV diagram can be used to explain how work will be done in

expansion and compression process of ideal gases

The area under a PV curve gives the magnitude of the work done on a system.

W<0 (W= -Ve) for compression and

W>0 (W= +Ve) for expansion.

P_i, V_i (initial state)

Process

P_f, V_f (final state)

PV diagram

❖ Work Depends on the Path way which the change have been occur.
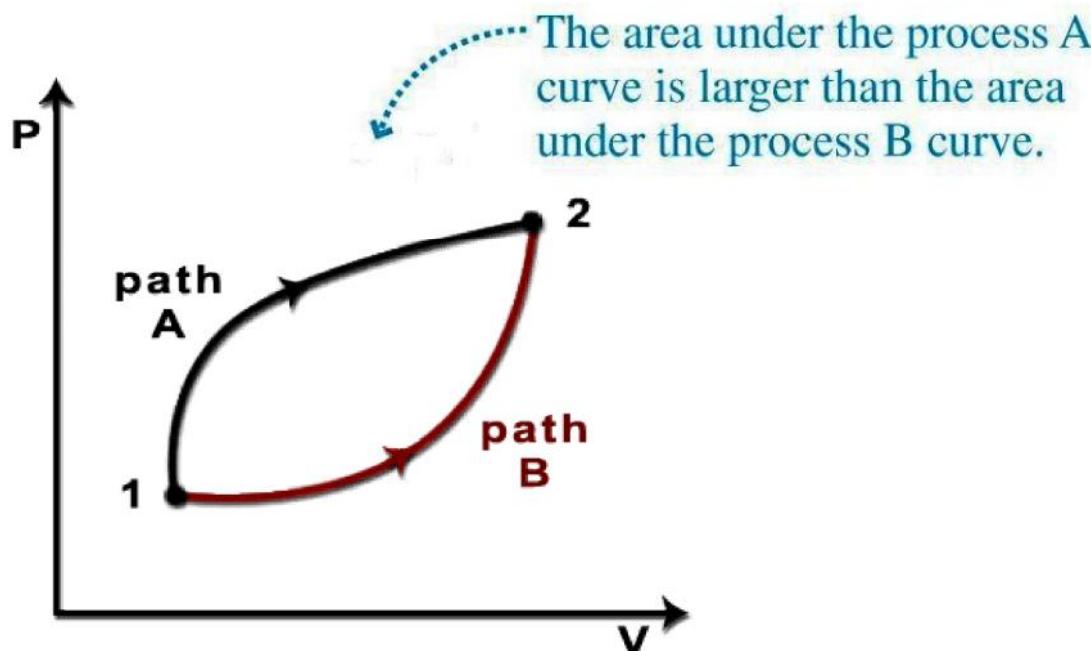
PV diagram

Adiabatic walls and Diathermal walls

Adiabatic walls

Insulating walls that do not permit heat to flow between the system and its surroundings are called *adiabatic walls.*

Diathermal walls

The system and its surroundings are separated by walls of some kind.

Walls that permit heat to flow through them, such as those of the engine block, are called **diathermal walls.**

Same temperature

A   B

Adiabatic walls

(a)

A   B

Diathermal walls
(silver)   (b)
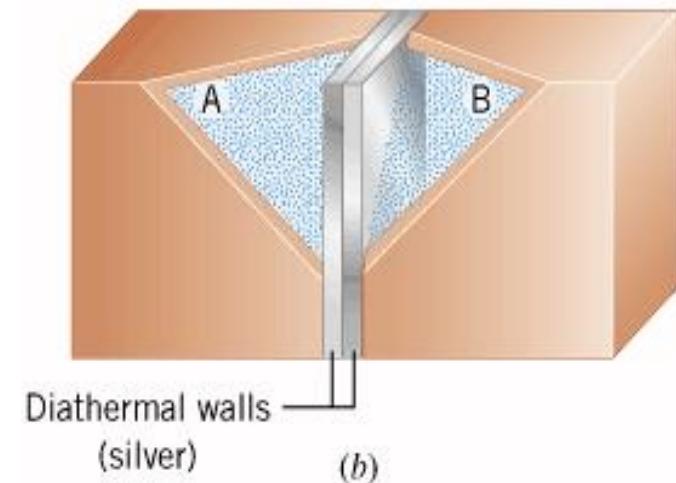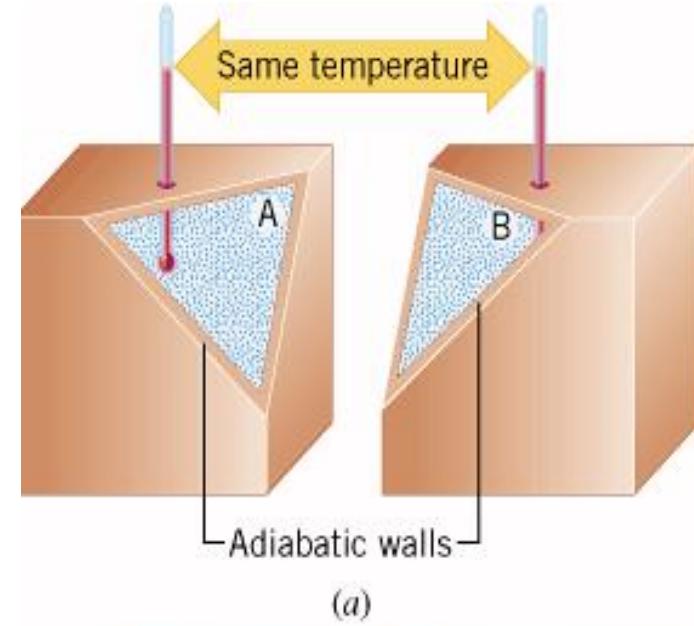
The Zeroth Law of Thermodynamics

If system A is in thermal equilibrium with

system C and system B in thermal equilibrium

with system C then system A and system B

have to be in thermal equilibrium.

No heat flows.

No heat flows
(A is in equilibrium with B)

No heat flows
(C is in equilibrium with B)

No heat flows
(A and C are found to be in equilibrium)
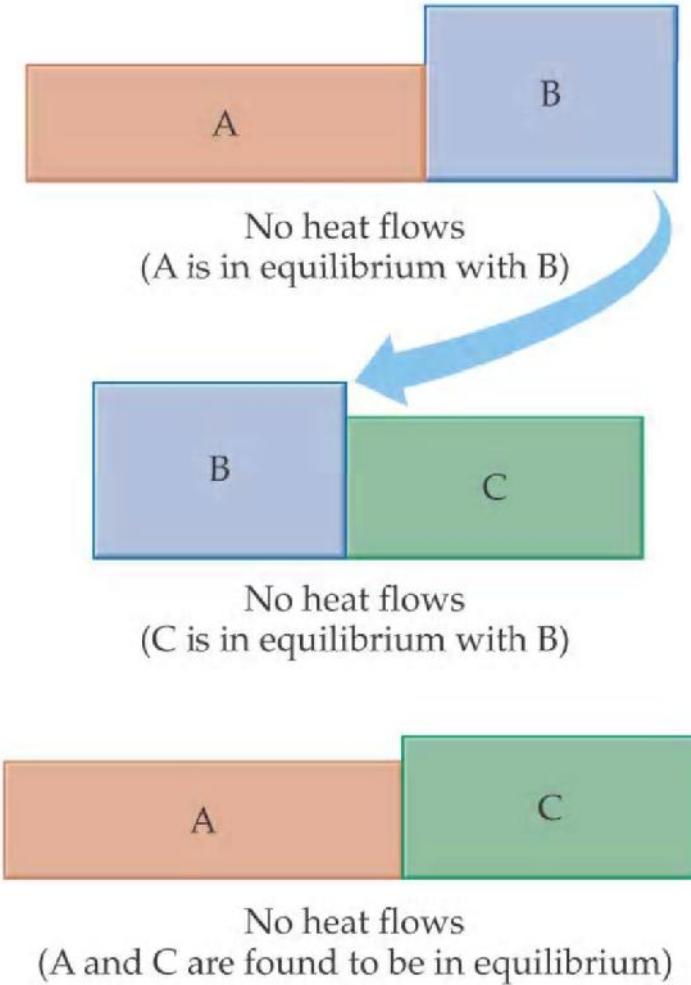
Fig. of (A, B and C System)

First law of thermodynamics

First law of thermodynamics

The states of first law thermodynamics is

" Energy may be converted from one form to another, but it is impossible to create or destroy it."

1. Isochoric Process (Constant Volume)

$$W = -\int_{V_i}^{V_f} p\,dV$$

$$W = -\int_{V_i}^{V_f} p\,dV = 0$$
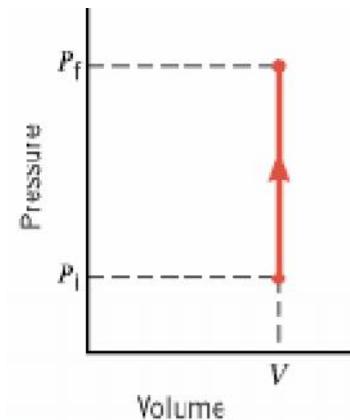
PV Diagram of Isochoric Process

Work Done $= 0$.

2. Isobaric Process (Constant Pressure)

$$W = -\int_{V_i}^{V_f} p\,dV = -p\int_{V_i}^{V_f} dV$$

$$= -p(V_f - V_i) = -p\Delta V$$

$W = -P \cup V$
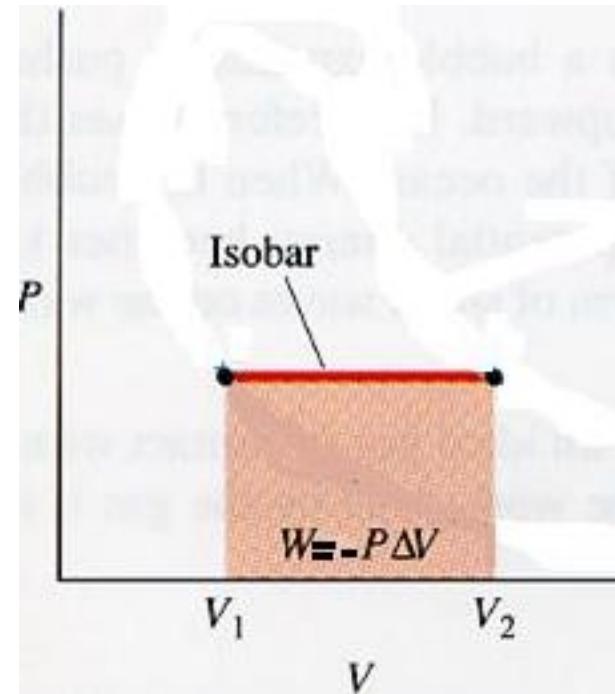
PV Diagram of Isobaric Process

3. Isothermal process (constant temperature) and the work done on an ideal gas

$$W = -\int_{V_i}^{V_f} pdV \quad \text{———①}$$

$$pV = NRT \quad \text{or} \quad p = \frac{NRT}{V} \quad \text{———②}$$

By substituting eq.(2) in eq.(1)
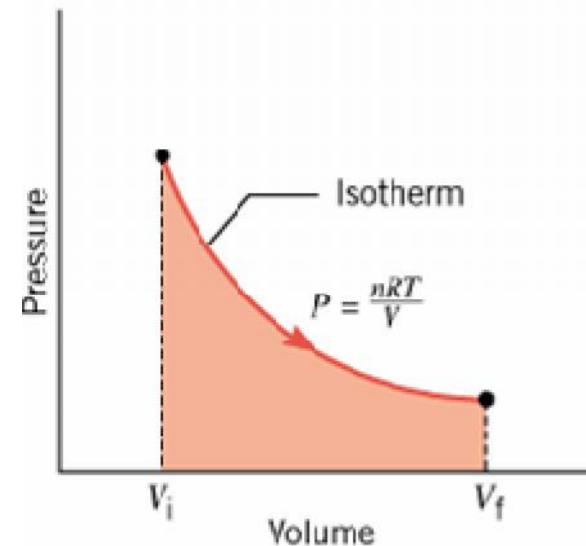
PV Diagram of Isothermal Process

$$= \int_{V_i}^{V_f} \frac{NRT}{V} dV \quad = NRT \int_{V_i}^{V_f} \frac{dV}{V} \quad \text{———} \quad \textcircled{3}$$

Taking integration eq.(3)

$$= NRT \ln V \quad = NRT \ln(V_f - V_i) = NRT \ln \frac{V_f}{V_i}$$

$$W = nRT \ln \left(\frac{V_f}{V_i} \right)$$

The above expression may be written as

$$W = nRT \ln \left(\frac{P_f}{P_i} \right)$$

$$\Delta U = Q - W$$

$$\Delta U = 0 \Rightarrow Q = W$$

Adiabatic processes

no heat is gained or lost by the system Q=0, i.e. system perfectly isolated.

$W = -P \cup V$

$\cup U = Q + W$

$Q = 0$

$\cup U = 0 + W$

$\cup U = W$
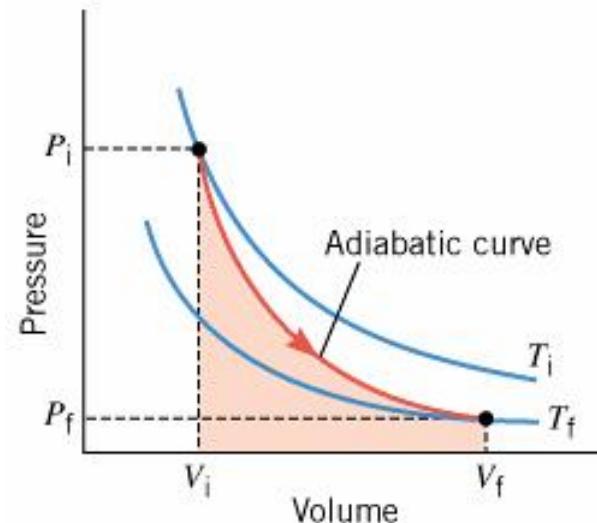
PV Diagram of Adiabatic Process

Enthalpy (H)

Defined as the amount of heat absorbed by the system at constant pressure provided that the only work done is of (pressure – volume).

$$\Delta H = H_2 - H_1 \quad Or \quad \Delta H = H_P - H_R$$

H_1 donated the initial value of enthalpy of the system and H_2 final value of the system.

H_R donated the enthalpy of reactants and H_P that of products.

Enthalpy is related to internal energy by following expression:

$$H = U + PV \ldots\ldots\ldots\ldots\ldots(1)$$

$$\Delta H = U_2 - U_1 + P_2V_2 - P_1V_1$$

$$\Delta H = (U_2 + P_2V_2) - (U_1 + P_1V_1)$$

$$\Delta H = (U_2 - U_1) + (P_2V_2 - P_1V_1)\ldots\ldots\ldots\ldots..(2)$$

If pressure maintained constant (i.e. $P_1 = P_2 = P$), eq.(2) becomes as follows:

$$\Delta H = \Delta U + P(V_2 - V_1)$$

Or

$$\Delta H = \Delta U + P. \Delta V$$

Or

$$\Delta H = q_p \text{ (because } q = \Delta U + P. \Delta V)$$

Sign of ∪H

i.   When the enthalpy of the reactants is greater than that of products (i.e. $H_R > H_P$), the energy will be given out to the surroundings and ΔH will carry a negative sign(- ve).

ii. If the enthalpy of the products is greater than that of reactants (i.e. $H_P > H_R$), the energy will be absorbed from the surroundings and ΔH will carry a positive sign(+ ve).

Heat capacity (C)

Defined as the quantity of heat required to raise the temperature of the system from the lower to higher temperature divided by the temperature difference.

If the mass of the system is one gram, the Heat Capacity is called the "Specific heat" and if the mass of the system is one mole, the Heat capacity called "molar heat capacity", is usually denoted by C.

The molar heat capacity of a system between temperatures T_1 and T_2 will be expressed as

$$C = q/(T_2 - T_1) \ldots\ldots\ldots (1)$$

As the heat capacity varies with temperature, hence the heat capacity defined by the differential equation

$$C = dq/dT \ldots\ldots\ldots (2)$$

Heat capacity (C)

The heat capacity of a gaseous system, determined at constant volume and pressure.

1) Heat capacity at constant volume (CV)

In tins case no external work is done by the system (W=0) since there is no change in the volume.

$$Cv = q/\Delta T \ldots\ldots(3)$$

Hence, from first law of thermodynamics equation

$$\Delta U = q + w \qquad W = 0$$

$$q = \Delta U \ldots\ldots\ldots\ldots(4)$$

By substituting eq.(4) in eq.(3)

$$Cv = (\Delta U /\Delta T)v$$
$$Or$$

$$\boxed{Cv = (\partial U /\partial T)v \ldots\ldots(5)}$$

Hence, the heat capacity at constant temperature defined as the rate of change of internal energy with temperature.

Heat capacity (C)

2) Heat capacity at constant pressure (CP)

In this case ther is change in the volume and some work is done. Suppose , the volume increase by ΔV and the work done is w. then, from first law of thermodynamics eq.

$$\Delta U = q + w \quad or \quad C_p = (q/\Delta T)_p \quad ………..(6)$$

Increase in volume means that work is done by the system on surrounding so that w is –Ve. Hence,

$$w = -p\Delta V ………..(7)$$
$$q = \Delta U - w ………………(8)$$

By substituting eq.(7) in eq.(8)

$$q = \Delta U - (- p\Delta V)$$
$$= \Delta U + p\Delta V ……..(9)$$

By substituting eq.(9) in eq.(6)

$$C_p = (\Delta U + p\Delta V /\Delta T)_p ……..(10)$$
$$\Delta H = \Delta U + p\Delta V = q ……………….(11)$$

By substituting eq.(11) in eq.(10)

$$C_p = (\Delta H /\Delta T)_p$$

Or

$$\boxed{C_p = (\partial H /\partial T)_p}$$

Hence, the heat capacity at constant pressure defined as the rate of change of enthalpy with temperature.

Relation between CP and CV in gaseous system

When a gas is heated at constant volume, no external work is done by the gas. All the heat supplied to the gas is used in increase its internal energy. Thus, if the temperature of one mole of gas is raised through 1°C (say from T to T+1), the increase the internal energy itself gives the molar heat capacity at constant volume.

However, when the gas is heated at constant pressure, there will be increase in its volume, the gas will expand and do some work. Hence, the molar heat capacity of gas at constant pressure must be greater than that at constant volume (i.e. $C_p > C_V$). The difference between two evidently, gives the work done by one mole of the gas in expansion when heated through 1°C at constant pressure. Thus,

$$C_P - C_V = W........(1)$$

(work done by one mole of the gas in expansion when heated through 1°C at constant pressure)

As we know, the work done by the gas in expansion at constant pressure is numerically given by $W = P\Delta V$.

For one mole of an ideal gas, $PV = RT$ …….(2)

When the temperature is raised by 1°C from T to T+1 so that the volume is V to V+ΔV, then $P(V+\Delta V) = R(T+1)$ ……..(3)

By opening the bracket in the eq.(3) becomes as follows

$PV + P\Delta V = RT + R$ ………(4)
By subtracting eq(2) from eq.(4) ,we get.
$PV + P\Delta V = RT + R$ ……(4)
$PV = - RT$ …….(2)   By subtracting

$P\Delta V = R$ …………..(5)

By substituting eq.(5) in eq.(1), we get
Hence, the work done by one mole of an ideal gas in expansion at constant pressure when heated through 1°C is equal to R.

$$\boxed{C_P - C_V = R}$$

Thus, the difference between the molar heat capacity of a gas at constant pressure (C_P) and constant volume (C_V) is equal to gas constant R.

Reversible Isothermal Expansion/Compression of Ideal Gas

Reversible isothermal expansion: maximum possible work

$$W = - nR \ln\left(\frac{V_f}{V_i}\right) = - nR \ln \frac{P_f}{P_i}$$

$\longrightarrow$ **W = - ve**
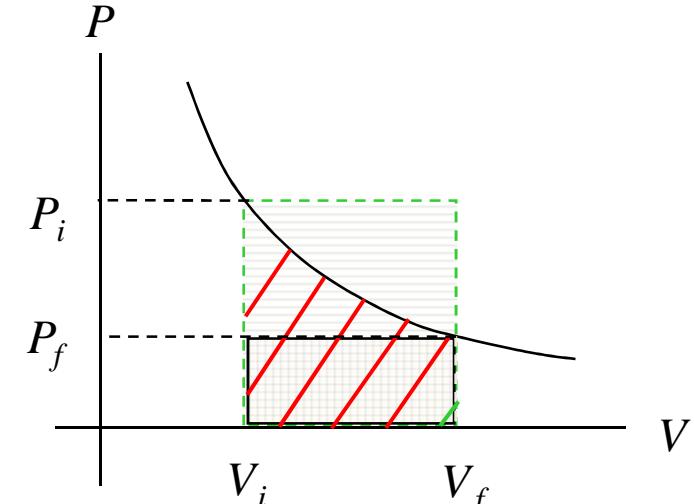
PV Diagram

Reversible isothermal compression: minimum possible work

$$W = - nR \ln\left(\frac{V_i}{V_f}\right) = - nR \ln \frac{P_i}{P_f}$$

$$W = nR \ln\left(\frac{V_f}{V_i}\right) = nR \ln \frac{P_f}{P_i} \longrightarrow \textbf{W = + ve}$$

Types of Irreversible isothermal expansion

1) Free expansion: Pext = 0 (the surroundings is a vacuum) Under these conditions, the work is always zero.

$$w = - \int_{V_A}^{V_B} P_{ext} dV = -P_{ext} \int_{V_A}^{V_B} dV = -P_{ext}(V_B - V_A) = 0$$

2) intermediate expansion: the volumes of the gas increase from V_A to V_B against a constant external pressure, $P_{Ext} \langle P$, the work done given by

$$w = - \int P_{ext} dV = -P_{ext} \int dV = -P_{ext}(V_B - V_A)$$

The final temperature in reversible adiabatic expansion can be calculated from the expressions which related the final and initial temperature to the respective volumes or pressure.

Let P be the external pressure against which expansion is taking place and ΔV be the increase in volume. Then the external work be done by the system is equal to -$p\Delta V$, hence according to first law equation,

$$\Delta U = q + w \qquad\qquad \text{(in adiabatic system q=0)}$$

$\Delta U = w = C_V = -p\Delta V\ldots\ldots(1)$

If ΔT is the fall in temperature, then, since $\Delta U = C_V\Delta T\ldots.(2)$

Substituting er.(1) in eq.(2) becomes
$C_V\Delta T = -p\Delta V\ldots.(3)$
For infinitesimally quantities, as in reversible expansion.

$PV = RT, P = RT/V\ldots\ldots\ldots(4)$

Substituting er.(4) in eq.(3) we get

$C_V\Delta T = - RT\ dV/V........ ..(5)$ \qquad\qquad (for one mole of gas)

$C_V \Delta T/T = - R \, dV/V$ ……..(6)   taking Lin for eq.(6) we get

$C_V d(\ln T) = - R d(\ln V)$………….(7) Integrating eq. (7) between temperatures T1 and T2 when the corresponding volumes are V_1 and V_2 we have

$C_V(\ln T_2/T_1) = - R \, \ln(V_2/V_1) = R \, \ln(V_1/V_2)$

$\ln T_2/T_1 = (R/C_V) \, \ln(V_1/V_2)$...........................(8)

knowing that $C_P - C_V = R$…………….(9)

by Multiply both side of eq.(9) by $(1/C_V)$ and putting $C_P/C_V = \gamma$ we get

$C_P/C_V - 1 = R/C_V$………(10)   Substituting er.(10) in eq.(8) we get

$\ln T_2/T_1 = (\gamma - 1) \ln(V_1/V_2) = \ln(V_1/V_2)^{\gamma - 1}$ by taking inverse ln for both side of we get,

$$\boxed{T_2/T_1 = (V_1/V_2)^{\gamma - 1}}$$ (Note that $\gamma > 1$)

Thus, since $V_2 > V_1$, $T_1 > T_2$ Hence , a cools during reversible adiabatic expansion.

The experimental technique used by Joule and Thomson for deriving the mathematical relation between the fall of pressure of a gas on expansion and the resulting lowering of temperature as shown scheme.
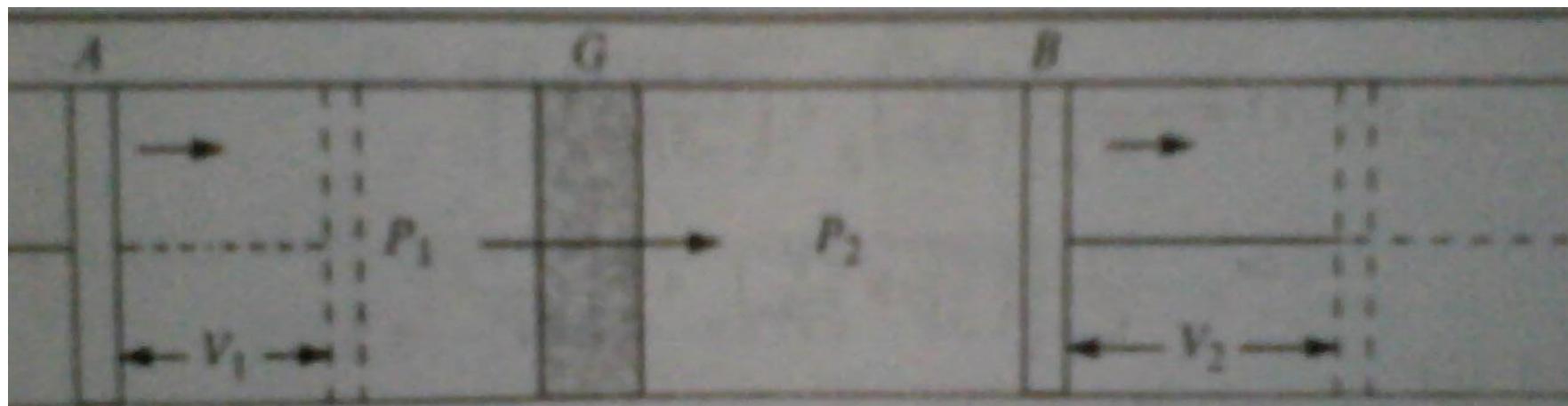

Fig.(2)

A tube made of a non-conducting material is fitted with a porous plug G in the middle and two pistons A and B on the sides, as shown, the tube thoroughly insulated to ensure adiabatic conditions.

A volume V_1 of the gas enclosed between the piston A and the porous plug G at constant P_1 is forced slowly through the porous plug by moving the piston A inwards and it allowed to expand to volume V_2 at a lower pressure P_2 by moving the piston B outward.

❖ Work done on the system at the piston A = + P_1V_1

❖ Work done by the system at the piston B = - P_2V_2

∴   Net work done by the system w_1 = - P_2V_2 + P_1V_1

Since the process is conducted adiabatically (i.e. q=0). Therefore, there is occur no exchange of heat between the system and surroundings, therefore performs work at the expense of the internal energy and its changes from U_1 to U_2.

$\Delta U = U_2 - U_1$.

The decrease of internal energy must be equal to net work done by W1.

- P_2V_2 + P_1V_1 = $U_2 - U_1$

$U_2 + P_1V_1 = U_1 + P_2V_2$

$H = U + PV$

$H_1 = H_2$

$\Delta H = 0$ (for adiabatic expansion)

Fro that we can concluded that these experiments are concerned with change in temperature with pressure at constant enthalpy   known as Joule-Thomson coefficient and denoted as $\mu_{J.T}$.

$$\sim_{\text{J.T}} = \left(\frac{\partial T}{\partial P}\right)_H$$

For real gas

Occur at constant enthalpy and known as isenthalpic process. Since H is a state function and taking H as a function of P and T.

$H = f(P,T)$ …….(1)

By taking differential for eq.(1), we get

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

On setting up the adiabatic condition demanded by Joule-Thomson effect.(i.e. dq=0)

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT = 0 \quad ……..(2)$$

Hence, $C_P = \left(\dfrac{\partial H}{\partial T}\right)_P$ ……..(3)

By substituting eq.(3) in eq.(2), we get

$dH = (\partial H/\partial P)_T dP + C_P\, dT = 0$

$dT/dP = - 1/C_P(\partial H/\partial P)T$

i.e $(\partial T/\partial P)H = - 1/C_P(\partial H/\partial P)T$………(4)

the quantity of $(\partial T/\partial P)H$ is called Joule-Thomson coefficient

assuming $\mu_{J.T}$ to be constant over a small pressure range and eq.(4) can be written as

$\Delta T = - 1/C_P(\partial H/\partial P)T \, \Delta P$ ……………(5)

Joule and Thomson verified the eq.(5) experimentally be accurately measuring the fall of the temperature (ΔT) accompanying the expansion of a number of real gas. In every case (ΔT) was found to be proportional to the (ΔP) on the two sides of porous plug. The Joule-Thomson expansion is one of the most important methods for liquefaction of gases.

For an ideal gas

Since H = U + PV, eq.(4) may be written as

$$\mu_{J.T} = - \frac{\partial(U + PV/\partial P)_T}{C_P}$$

$$\mu_{J.T} = - \frac{1}{C_P} (\partial U/\partial P)_T + (\partial PV/\partial P)_T$$

$$\mu_{J.T} = - \frac{1}{C_P} (\partial U/\partial V \times \partial V/\partial P)_T + (\partial PV/\partial P)_T$$

For an ideal gas $(\partial U/\partial V)_T = 0$

$$(\partial U/\partial V \times \partial V/\partial P)_T = 0$$

Also, since for an ideal gas PV is constant at constant temperature,

$$(\partial PV/\partial P)_T = 0$$

Hence, in eq.(6) $\mu_{J.T} = 0$.

Sign of $\mu_{J.T}$

+ ve when implies cooling on expansion.

– ve when implies warming on expansion.

Relation between Enthalpy and Internal Energy

The precise definition of enthalpy, H, is

H = U + PV

Many reactions take place at constant pressure,

so the change in enthalpy can be given by

Δ H = Δ U + PΔV

Rearranging:

Δ U = ΔH − P Δ V

The term (–PΔV) is the energy needed

 to change volume against the atmospheric pressure,

P. It is called pressure-volume work.
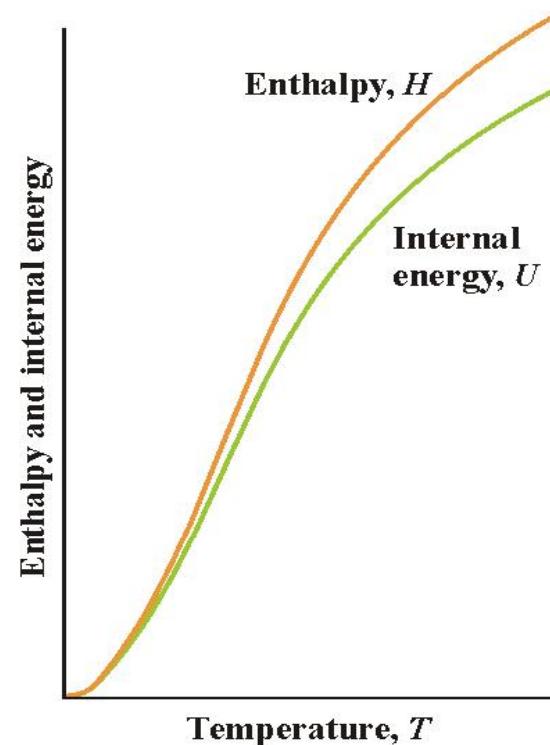
Fig.(3)

Examples on Thermodynamics

Example (1)

one mole of an ideal gas expand against a constant pressure of 1 atm from a volume of 10L to 30L. Calculate the work done by the gas in joules.

Answer:

W = - 2027 J

Example (2)

A gas expands isothermally against a constant external pressure of 1 atm from 2L to 5000ml. in this process it absorbs 200J of thermal energy from its surroundings.

Calculate ΔU for the process in joules.

Answer = - 104 J

Example (3)

Six moles of an ideal gas expand isothermally and reversibly from 1L to 10L at 27°C.

what is the maximum work done by joules.

Answer = - 34419 J

Example (4)

Prove that in an isothermal expansion of one mole of an ideal gas

$$\Delta U = 0$$

$$\Delta H = 0$$

Example (5)

H.w

Calculate the final volume of one mole of an ideal gas initially at 0°C and 1 atm if it absorbs 1000 cal of heat during a reversible isothermal expansion.

Answer = 141.25 L

Example (6)

one mole of an ideal gas (monatomic) at 27°C expands adiabatically against a constant external pressure of 1 atm from a volume of 10L to 20L.

Calculate q, w, ΔU and ΔH for this process. Also calculate the final temperature of the gas.

Example (7)

H.w

Two moles of the monatomic gas argon expand isothermally at 298K

from and initial volume of 0.025m3 to a final volume of $0.050m^3$.

 Assuming that argon is an ideal gas,

find (a) the work done by the gas,

(b) the change in internal energy of the gas,

(c) the heat supplied to the gas.

Example (8)

How much heat is required to rise the temperature of one mole oxygen from 300K to 1300K at constant pressure.

$C_P = 6.095 + 3.253 \times 10^{-3}\ T - 1.017 \times 10^{-6}\ T^2$

Answer = 7720.8 cal/mol

Example (9)

Calculate work done by KJ when 65.38g of zinc dissolves in hydrochloric acid in case

 a) closed beaker .

b) open beaker at 300K.

Example (10)

For CO2 (g) at 300K and 1 atm $(\partial H/\partial P)_T = 10.2$ cal.mol^{-1}.atm^{-1} and

$C_P = 8.919$ cal.mol^{-1}.deg^{-1}.

Calculate the Joule-Thomson coefficient of gas for the given temperature and pressure condition.

Answer = 1.1436 deg. atm^{-1}